



Hydrogen catalytic effects of nanostructured alloy particles in spent fuel on radionuclide immobilization

D. Cui^{a,b,*}, J. Low^a, V.V. Rondinella^c, K. Spahiu^d

^a Studsvik AB, 61182 Nyköping, Sweden

^b Stockholm University, Dept. of Material and Environmental Chemistry, 10691 Stockholm, Sweden

^c European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany

^d Swedish Nuclear Fuel and Waste Management Co., 10124 Stockholm, Sweden

ARTICLE INFO

Article history:

Received 13 August 2009

Received in revised form 31 October 2009

Accepted 7 November 2009

Available online 13 November 2009

Keywords:

Radioactive catalyst

Nanoparticle

Hydrogen

Fission product

Nuclear waste

ABSTRACT

For the first time, hydrogen catalytic effects of fission product alloy particles nondestructively extracted from spent nuclear fuel were demonstrated. The redox sensitive radionuclides at oxidized forms Se(IV), Tc(VII), U(VI), Np(V) and Pu(VI) were found to be stable in a solution saturated with a gas mixture (Ar + 10% H₂ + 0.03% CO₂) but rapidly immobilized in the same solution when contacted with the particles. In comparison, a synthetic alloy sample with similar elemental composition as the alloy particles generated in nuclear fuel displayed a smaller, but unequivocal catalytic effect. The smaller catalytic effect of synthetic alloy was apparently enhanced by a β -radiation source. The information obtained in this work contributes to improved understanding of the redox chemistry of radionuclides in nuclear waste geologic repository environments and, in particular, of the catalytic properties of these unique alloy particles.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Catalyst science and technology has been widely applied in environmental engineering, but seldom considered for application in the design of nuclear waste repository. The direct disposal of spent nuclear fuel (SNF) as a waste form is currently under consideration in several countries. In most disposal concepts, SNF will be encapsulated in canisters made of or containing large amounts of iron, surrounded by compacted bentonite clay and placed in deep repositories built at several hundred meters depth. In the safety assessment, it is conservatively assumed that groundwater will enter through clay buffering material and waste canisters and contact SNF within a timeframe of >1000 years, and leaching and migration behaviors of radionuclides that contained in SNF need to be evaluated. In typical anaerobic groundwater in deep granite (characterized by pH 8.5, ~10 mM ion strength and 2 mM NaHCO₃), UO₂ as matrix (>90 wt.%) of SNF is expected to be oxidized due to oxidative species produced by water radiolysis and dissolved by forming carbonate complex U(VI)O₂(CO₃)₂²⁻. The dominating speciation of long-lived actinides ²³⁷Np (*t*_{1/2} 2.14 × 10⁶ a) and ²³⁹Pu (*t*_{1/2} 2.40 × 10⁴ a) dissolved from SNF will

be in form of carbonate complexes Np(V)OCO₃⁻, NpO₂(CO₃)₂³⁻ and Pu(VI)O₂(CO₃)₂²⁻, respectively, while long-lived fission products ⁹⁹Tc (*t*_{1/2} 2.11 × 10⁵ a) and ⁷⁹Se (*t*_{1/2} 2.95 × 10⁵ a) will be in the form of anions Tc(VII)O₄⁻ and Se(IV)O₃²⁻ or Se(VI)O₄²⁻, respectively [1]. Sorption and precipitation of these carbonate complexed and/or negatively charged radionuclide species on negatively charged mineral and metal surfaces at nominal groundwater pH (8–9) are thermodynamically unfavorable. After all the oxygen which ingress the repository during the excavation and waste emplacement phases is consumed and outer protective layer of canister (copper in Swedish design) damaged, it is expected that hydrogen overpressure will be generated in the deep repository due to the anoxic corrosion of the massive iron canister material by groundwater. Dissolved hydrogen is chemically inert below ~100 °C; however, in presence of catalytic surfaces it could significantly contribute to establishing stronger reducing conditions in the region surrounding the spent fuel containers (near field), thus reducing radionuclides to their nearly insoluble forms NpO₂, PuO₂, TcO₂, Se(0) or Se(–I) [2], and dramatically limiting the overall corrosion of the SNF matrix. Besides other potential catalyst materials, such as fuel cladding and canister materials, the alloy particles composed by fission products Mo, Ru, Tc, Pd, Rh and Te present in SNF could be particularly effective as catalysts. These 4d-transition metals alloy particles constitute one of the main forms of fission products in SNF [3]. In spite of their low mass fraction in SNF (0.2–0.7%), submicro-nano-sized 4d-metal-particles are present in

* Corresponding author at: Studsvik Nuclear AB, Hot Cell Lab, Studsvik, 61182 Nyköping, Sweden. Tel.: +46 155 221676; fax: +46 8 155 263156.

E-mail address: daqing.cui@studsvik.se (D. Cui).

large numbers at the rim of SNF and in UO_2 grain boundaries [4], are thus expected to contribute substantially to prevailing beneficial reducing conditions thanks to their catalytic properties in hydrogen saturated conditions. In a previous electrochemical investigation [5], a simulated SNF material, $\text{UO}_2(\text{s})$ containing stable elements simulating fission products, including Mo–Ru–Pd–Rh micro-particles, was found to display a much lower corrosion potential than pure $\text{UO}_2(\text{s})$ in H_2 purged solution. The observation of the very small dissolution rate of SNF in hydrogen saturated solution suggests that the existence of effective hydrogen catalyst on SNF surface [6].

A non-oxidative method of extracting 4d-metal alloy particles from SNF has been recently developed [7,8]. It is based on the strong complexation of U(IV) by concentrated H_3PO_4 [9] making possible the dissolution of the fuel matrix without the use of strongly oxidizing HNO_3 . The compositions of 0.5–1.0 μm sized and 10–20 nm sized alloy particles are 32.7Mo–40.5Ru–7.0Tc–11.7Pd–4.2Rh–3.9Te and 26.5Mo–32.7Ru–7.6Tc–23.2Pd–6.3Rh–3.9Te, respectively. The TEM electron diffraction pattern of a 15 nm sized particles is similar with that the X-ray diffraction pattern of the whole extracted residues. The result of EXAFS analysis showed that the extracted particles are a “true alloy”, much more homogeneous than synthetic alloy with similar nominal composition [8]. The results of leaching tests on the extracted alloy particles showed that Tc, Mo and Te were leached out from the alloy particles in a Ar-purged simulated solution (10 mM NaCl + 2 mM NaHCO_3) due to the β -radiolysis of water. When the purge gas was changed to Ar + 10% H_2 mixture, the concentrations of all nuclides decreased rapidly. This was explained by the hydrogen induced reductive precipitation of Mo, Tc and Te with the help of 4d-metal particles as catalyst [8].

Adsorption and desorption of reactants on a catalyst surface can directly affect its catalytic ability to hydrogen oxidation. If H adsorption enthalpy is too small, a slow H adsorption kinetic will limit the rate of the overall reaction; If the H adsorption enthalpy is too high, the desorption of H becomes difficult. Platinum group 4d-transition metals, including Ru, Pd and Rh contained in the extracted fission product particles, have intermediate values of H adsorption enthalpy and therefore display higher catalytic activities for hydrogen oxidation [10] and should play a very important role on controlling the stabilities of redox sensitive radionuclides in SNF at the repository environment.

The main objective of this work is to prove if oxidized species of the redox sensitive nuclides ^{238}U , ^{237}Np , ^{239}Pu , ^{99}Tc and ^{79}Se can be reductively immobilized by H_2 alone or if the combined action of H_2 as reductant and 4d-metal particles as catalysts is necessary. Several works on interfacial radiolysis [11–13] have shown that the interaction of radiation with solid oxides can make possible specific reactions at their surface mediated by the radiation energy deposited in the solid. The enhancing effect of β -radiation on catalyzed redox reactions has also been observed [14,15]. For this reason the influence of β -radiation from a ^{90}Sr source on the catalytic effect of a synthetic stable alloy with similar composition was investigated. In order to compare our results with a well known reductive surface, the rate of hydrogen induced radionuclide reduction/immobilization is compared with the corresponding process on reductive iron canister material.

2. Experimental

2.1. Solutions

It is known that sorption and precipitation of negatively charged oxidized forms of radionuclides (as described in Section 1)

on glass and metal surfaces in an acidic solution (pH 3) are insignificant. The solubilities of reduced forms of these radionuclides lie within the range of 10^{-7} to 10^{-9} M and are independent from pH in the range of pH 3–10 [16,17]. To study the redox behaviors of the radionuclides contained in a solution while avoiding the influence of adsorption, the first series of experiments was conducted at pH 3.0 (solution (a)). In a second series of test, the immobilization processes of redox sensitive radionuclides in the solution (b), similar with the groundwater expected in the near field of a granite repository (pH 8.5, 10 mM NaCl + 2 mM NaHCO_3), without adding any solid surfaces or with the presence of extracted fission product particles and other reference materials were investigated.

Two solutions (a) and (b) were prepared, containing 10 mM NaCl + 2 mM NaHCO_3 and the following radionuclides:

- (a) 10^3 ppb U(VI), 10^2 ppb Pu(VI), Np(V) and Tc(VII), pH 3.0.
- (b) 10^3 ppb U(VI), 10^2 ppb Pu(VI), Np(V) and Se(IV), pH 8.5.

The solution (b) will be labeled as simulated groundwater solution. The redox behavior of ^{99}Tc in 10% H_2 purged solution at normal groundwater pH (8.5) with the presence of extracted alloy particles has been previously investigated [8]. Therefore, in solution (b) Tc is replaced by the stable element Se(IV) to simulate another long-lived fission product, ^{79}Se . Np(V) and Pu(VI) in solutions (a) and (b) are obtained from standard ^{237}Np (V) and ^{239}Pu (VI) solutions in 2 M HNO_3 after removing oxidative nitrate and adjusting pH. By using a multi-nuclide “cocktail” solution for the study of the near field behavior of radionuclides instead of single radionuclide solutions, it is possible to get information about sequences of reducing reactions for different radionuclides while somewhat simplifying the experimental set-up and the solution analysis. All radionuclides are initially in their oxidized form, excluding thus the possibility of redox reactions occurring among redox sensitive radionuclides in solution.

2.2. Solids

2.2.1. Extracted fission product alloy particles

5.5 mg of particles extracted from SNF that experienced high temperature (linear power 20 kW/m) with low burnup (23 MW d/kg U) by the recently developed nondestructive H_3PO_4 method [7] was used in the batch experiments. This extraction method avoids altering the particles due to oxidative acidic dissolution, as in the case of standard SNF reprocessing method using nitric acid. A SEM image of the extracted alloy particles on the glass-fiber-filter used in the extraction procedure and TEM image of a fine particle aggregate are given in Fig. 1(a) and (b). It shows that the extracted particles are composed by 0.5–1 μm sized sub-micrometer particles and aggregated 10–20 nm alloy particles. The average composition of the bigger fission product alloy particles (0.5–1 μm) was analyzed by SEM–WDS to be 32.7% Mo, 40.5% Ru, 7.00% Tc, 4.2% Rh, 11.7% Pd, 3.8% Te, and that for 10–20 nm sized alloy particles was analyzed by TEM–EDS to be 29.7% Mo, 27.0% Ru, 12.1% Tc, 4.6% Rh, 24.0% Pd, 2.3% Te.

2.2.2. Synthetic alloy

To evaluate the catalytic effect of the nanostructured fission product alloy particles extracted from SNF, a synthetic alloy with similar elemental composition, but without radioactive ^{99}Tc , was synthesized. Metal powders were supplied by the Johnson Matthey Company, with at least 99.99% purity. The metal powders were compressed to pellets of 1 cm diameter, with element weight ratio 46% Mo, 29% Ru, 21% Pd, 4% Rh. The metal pellets were melted at

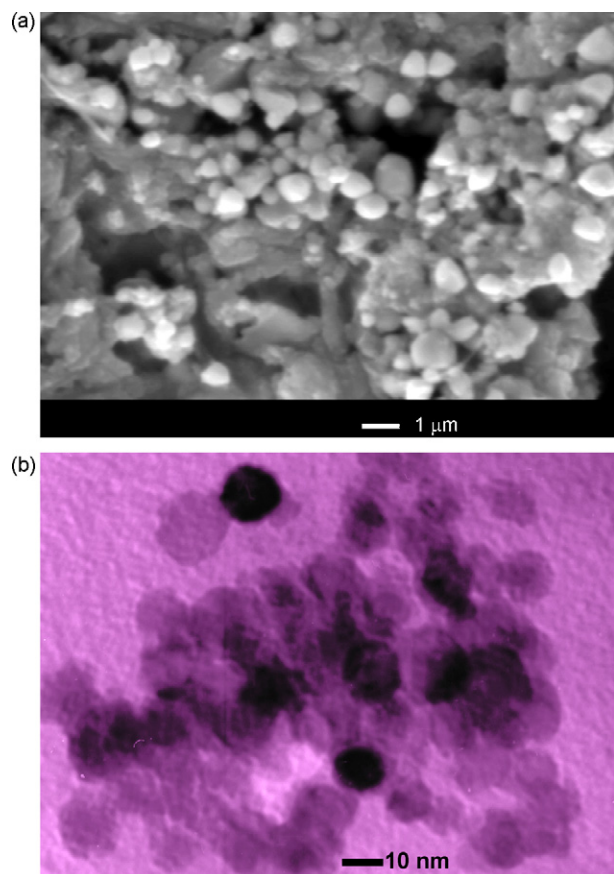


Fig. 1. Microscopic images of fission product particles extracted from SNF. (a) SEM image of the extracted particles deposited on glass-fiber-filter. The light colored 0.1–1 μm sized alloy particles and dark grey colored aggregates of very fine particles. (b) TEM image of a cluster of 10–20 nm sized particles (as the dark grey aggregate shown in the SEM image a).

about 1800 $^{\circ}\text{C}$ by cold crucible levitation melting method under Ar gas flushing. Afterwards they were annealed in Ar at 1511 $^{\circ}\text{C}$ (with 4 $^{\circ}\text{C}/\text{min}$ heating and cooling rates). Small and thin discs of the synthetic alloy (ca 0.3 mm thick with $\sim 1.0\text{ cm}^2$ surface area) were prepared and used in a parallel experiment. From the particle size observed in Fig. 1 it can be estimated that the surface area of 5.5 mg extracted alloy particles is many times larger than that of the synthetic alloy. Given the high radioactivity of the extracted particles, a direct measurement of their specific surface area (e.g. by BET) is not feasible.

2.2.3. Synthetic alloy with β -source

To evaluate the potential influence of β -radiation from the radionuclides (β -emitters) ^{99}Tc , ^{106}Ru and ^{107}Pd contained in the alloy particles on the hydrogen catalytic effect of the alloy particles, a ^{90}Sr source with 370 kBq activity was used in the experiment with the synthetic alloy. The back side of the aluminum substrate for the β -source was coated by epoxy. The sorption of radionuclides on the epoxy surface was proved through a separate batch experiment to be insignificant. The β -source was placed at a distance of about 0.1 mm from the surface of a synthetic alloy slice. The back side and the lateral surface of the synthetic alloy slice were coated by epoxy, with only the front face exposed to the water and the β -source. The effective water contacting alloy surface area was about 0.35 cm^2 .

2.2.4. Iron coupon

To evaluate the relative scales of the hydrogen catalyst effect of fission product alloy particle (Section 2.2.1) and the reducing effect

Table 1

Experimental matrix.

Experiment series solutions and pH	1	2
	(a) 1 ppm U, 0.1 ppm Np, Pu, Tc, pH 3.0	(b) 1 ppm U, 0.1 ppm Np, Pu, Se, pH 8.5
Blank	1a	2a
Extracted particles, 5.5 mg	1b	2b
Synthetic alloy 1 cm^2	1c	
Synthetic alloy 0.35 cm^2 + β	1d	
Iron 1 cm^2	1e	2c

of iron waste canister on the radionuclide immobilization at repository environment, a polished 1 cm^2 Fe-coupon with 99.99% purity was used as a reductant in an additional batch experiment for comparison.

2.3. Experimental set-up

The array of two series of eight batch experiments with pH 3.0 and 8.5 is described in Table 1. These batch experiments were performed at room temperature ($22 \pm 2\text{ }^{\circ}\text{C}$) in 20 mL simulated groundwater solution in 25 mL sized reaction vessels. The leaching vessels were placed in a larger controlled atmosphere container purged with anaerobic gas mixture, as described previously [18]. The gas mixture used in this work was Ar + 10% H_2 + 0.03% CO_2 (as stabilizer for 2 mM HCO_3^- concentration at pH 8.5). An oxygen trap with FeCO_3 and CaCO_3 [18] was placed in the larger vessel to further control the oxygen content. The extracted fission product alloy particles on the glass-fiber-filter were transferred in a leaching vessel in the controlled atmosphere container. The solution samples, taken using a syringe and passing the needle through a rubber-membrane-screw-cap, were centrifuged at 12,000 rpm for 30 min, weighed by analytical balance and analyzed by ICP-MS. All experiments were conducted at a radiochemistry laboratory with special cares of radiation protection.

3. Result and discussion

3.1. Batch experiments at pH 3.0

The evolution of U, Np, Pu, Np and Tc concentrations with reaction time in five experiments (1a–1e Table 1) with the cocktail solution (a) (pH 3.0) are shown in Fig. 2.

3.1.1. Blank experiment, 1a

All radionuclide concentrations are stable in solution in the experiment without any solid surface except glass vessel wall, e.g. U(VI) 960 ± 13 ppb during the whole experimental period, 28 days. This means that experimental errors in sampling and ICP-MS analysis are rather small around $\pm 1.4\%$. It also indicates that Tc(VII), U(VI), Np(V) and Pu(VI) can be neither sorbed on vessel wall nor reduced by 0.1 atm hydrogen without the presence of catalyst.

3.1.2. Extracted alloy particles, 1b

In the experiment with the extracted alloy particles, $>97\%$ Tc(VII), U(VI), Np(V) and Pu(VI) were disappeared from solution after one week reaction time. The adsorption under such acidic conditions is not significant (as confirmed in the blank experiment); therefore, it can be concluded that all these radionuclides can be reduced by 10% H_2 in the presence of the extracted alloy particles. It should be noted that the extracted particles contribute also to the source terms of Tc(VII). Most of the initially measured 1000 ppb Tc(VII) in solution were leached

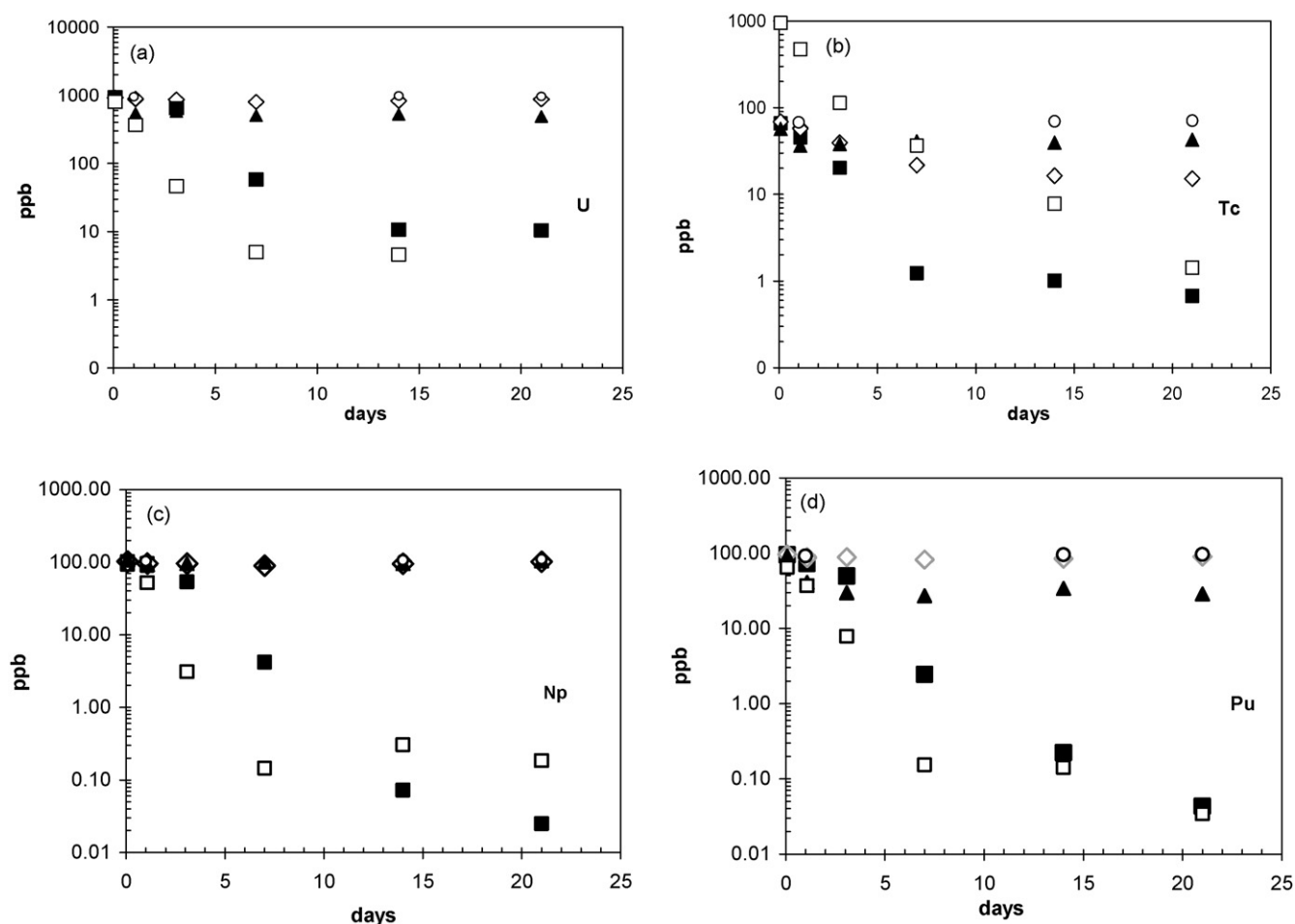


Fig. 2. The evolution of U, Tc, Pu, Np concentrations with reaction time in different experiments at pH 3: (○) blank experiment without any solids; (◇) synthetic alloy; (▲) synthetic alloy with β -source; (□) extracted alloy particles (note that the extracted particles are source terms of Tc); (■) iron coupon. The percentage of radionuclides immobilized by hydrogen after two weeks reaction time in experiments 1c and 1d is: U: (1c, ◇) 12.5%, (1d, ▲) 49%; Tc: (1c, ◇) 75%, (1d, ▲) 42%; Pu: (1c, ◇) 10.6%, (1d, ▲) 64%; Np: no significant immobilization in both cases.

from the extracted particles before purging with the Ar–H₂ gas mixture.

3.1.3. Synthetic alloy, 1c and synthetic alloy with β -source, 1d

The drops of radionuclide concentrations (ppb in log scale) in experiments 1c and 1d after two weeks reaction time are described in the text to Fig. 2.

This observation indicates that the synthetic alloy has some catalytic effect on H₂-induced reduction of U(VI), Pu(VI) and Tc(VII).

The dose rate at the location of the synthetic alloy in the batch experiment, 0.1–0.2 mm apart from the 370 kBq ⁹⁰Sr source, is estimated to be about 1 mGy/h. Considering the difference of water contacting surface areas of alloy slices in these two experiments 1c (1.0 cm²) with β -source and 1d (0.35 cm²) with β -source, U(VI), Pu(VI) reduction reactions were, respectively, 10–20 times faster in experiment 1d than that in experiment 1c. This would indicate that the catalytic effects of synthetic alloy for U(VI), Pu(VI) reduction can be enhanced by β -irradiation. Furthermore, in these two experiments, Tc(VII) was immobilized much faster than the three actinides. Taking into account the difference in water contacting surface areas in the experiments 1c and 1d, it looks like that β -radiation has no significant influence on the catalytic effect of the synthetic alloy on hydrogen induced Tc(VII) reduction-immobilization. Perhaps, the catalytic effect of the synthetic alloy on the Tc(VII)–H₂ reaction has already reached its “maximum” value in experiment 1c; in other words, the reaction rate is determined by

other kinetic controlling steps such as diffusion. The average distance of β -particles from ⁹⁰Sr in water is about 8 mm. The β -source with the small dose rate may only affect the catalytic effect of the synthetic alloy, but should not significantly affect the chemistry of the solution. If there was any effects of radiolysis, this effect would make the solution more oxidative, i.e. more difficult for radionuclide reduction and immobilization. In fact, it was observed that the combined effect of β -radiation and synthetic alloy under the atmosphere with 10% hydrogen significantly enhanced the reductive immobilization of radionuclides.

The stronger catalytic effect of extracted alloy particles on hydrogen induced immobilization of U(VI), Pu(VI) and Np(V) observed in the experiment (1b), as compared to that of synthetic alloy surfaces (1c and 1d) may be explained by the larger solution contacting surface area and/or nanostructure of the extracted alloy particles. Since the 5.5 mg extracted particles contained small amounts of oxides of fission products [8] and since the specific surface area of the extracted alloy particles has not been measured, it is not possible in the present work to quantify the catalyst effect per unit surface area of the extracted alloy particles.

3.1.4. Iron coupon, 1e

As expected, polished iron can effectively reduce Tc(VII), U(VI), Np(V) and Pu(VI) and immobilize them. However, these oxidized radionuclide species can be reduced and immobilized much more rapidly by 10% H₂ in presence of the extracted alloy particle catalyst (1a) compared to the case with the polished iron coupon.

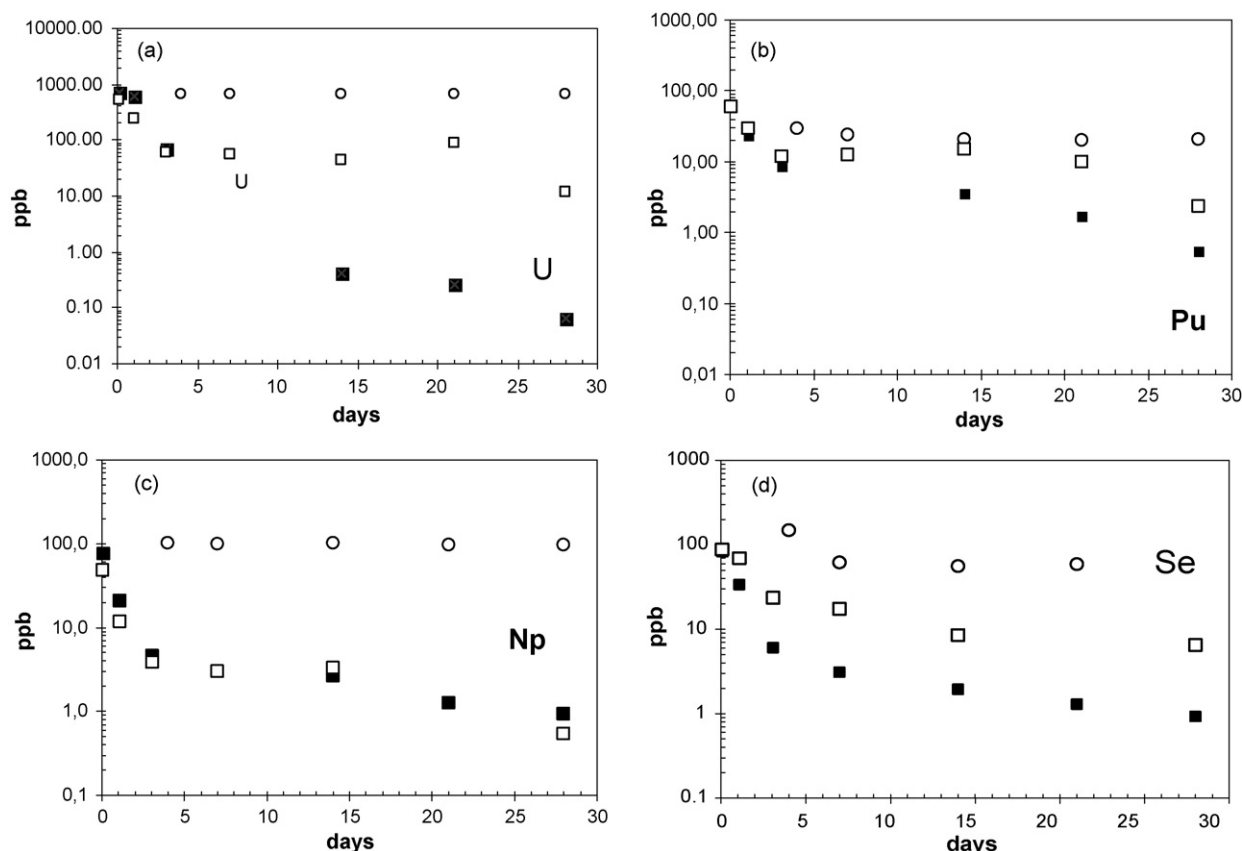


Fig. 3. The evolution of U, Pu, Np, Se concentrations with reaction time in different experiments at pH 8.5. The data for experiments with different solid surfaces are shown by the following symbols: (○) blank experiment; (□) extracted alloy; (■) iron coupon.

U(VI), Np(V) and Pu(VI) concentration in experiment (1b) in the first week dropped to levels 10 times lower than that in experiment 1e. The final radionuclide concentrations in experiment 1e may be influenced by the sorption on the iron oxides. Tc(VII) concentrations in experiment 1b (with extracted alloy particles) and that in 1e (with iron) are not comparable because the extracted alloy particles contain 12% ^{99}Tc , and the Tc concentration in experiment 1b is a balanced value of two parallel processes oxidative dissolution from the radioactive particles and hydrogen induced reductive immobilization of Tc from solution.

3.2. Experiments at pH 8.5

The behavior of the redox sensitive nuclides (U, Pu, Np and Se) in the simulated groundwater solution (pH 8.5) was investigated in the second series of experiments with cocktail solution (b) (see above Section 2.1 and Table 1). The observed variations of radionuclide concentration with time in the different experiments are summarized in Fig. 3, and discussed below:

3.2.1. Uranium

Blank experiment, 2a: the U(VI) concentration is stable at 651 ± 11 ppb in 10% hydrogen purged 10 mM NaCl, 2 mM NaHCO_3 solution at pH 8.5. It means that the U(VI) carbonate complexes are neither adsorbed by the wall of the glass vessels nor reduced by the dissolved H_2 by any measurable extent.

Experiment with the extracted alloy particles, 2b: the initially added U(VI) concentration was reduced from 651 to 10 ppb after 28 days, clearly showing the catalytic effect of extracted alloy particles.

Experiment with metallic iron 2c: the iron added to the reaction bottle can reduce U(VI) with similar kinetics as the H_2 -induced

U(VI) reduction in presence of extracted alloy particles: U(VI) concentration dropped to 6 ppb after 28 days of reaction.

3.2.2. Plutonium

Blank experiment, 2a: the Pu(VI) concentration dropped from 70 to 23 ppb during the first week of test and was stabilized at 20 ppb after 28 days. This observation is in a agreement with the reported instability of Pu(VI) at neutral pH [19,20]. In absence of strong oxidants, Pu(VI) is reduced by water to Pu(V) which can be disproportioned to Pu(VI) and Pu(IV) [21]. The precipitation of low solubility Pu(IV) oxide [19] may explain the concentration decrease.

Experiment with the extracted alloy particles, 2b: the initially added 70 ppb Pu(VI) were reduced to 10 ppb after 3 days, and to 3 ppb level after 28 days, indicating a strong effect associated with the fission product alloy particles.

Experiment with metallic iron, 2c: the iron added to the reaction bottle reduced Pu(VI) with an even faster kinetics. The total Pu concentration dropped to 0.3 ppb level, or 1×10^{-9} M during the experiment. This decrease must be associated with immobilization of Pu in corroded iron phases at the iron coupon surface [22].

3.2.3. Neptunium

Blank experiment, 2a: the Np(V) concentration in solution was very stable, 99 ± 2 ppb during the whole experimental period of 28 days.

Experiment with extracted alloy, 2b: the initial 99 ppb Np(V) was reduced to 0.6 ppb after 28 days.

Experiment with metallic iron, 2c: the iron added to the reaction bottle reduced Np(V) to NpO_2 ; the total Np concentration in solution dropped to 1 ppb.

3.2.4. Selenium

Blank experiment, 1a: Se(IV) concentration dropped from 90 to 60 ppb after 7 days of reaction, and stabilized during the rest of the experiment. This indicates that Se(IV) can be slightly sorbed or precipitated under the experimental conditions adopted.

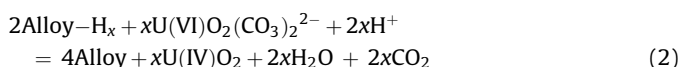
Experiment with extracted alloy, 2b: the alloy particles extracted from SNF act as catalysts for the hydrogen induced Se(IV) reductive immobilization. Se concentration dropped from 90 to 6.5 ppb during the test.

Experiment with metallic iron, 2c: The iron added to the reaction bottle can reduce Se(IV) to Se(0) or Se(−I) (as FeSe₂); during the test the concentration dropped from 90 to 0.6 ppb level. This observation agrees with recently reported results [23] and confirms that iron canister material can work as stronger reductant to immobilize the redox sensitive radionuclide, ⁷⁹Se.

From these experiments (2a, 2b and 2c), it is demonstrated that redox sensitive radionuclides (U(VI) Np(V) Pu(VI) and Se(IV)) can be reduced by dissolved H₂ under catalytic effect of 4d-metal particles in simulated groundwater solution (2 mM HCO₃[−], pH 8.5 and purged with Ar + 10% H₂ + 0.03% CO₂ gas mixture).

3.3. Possible mechanism of hydrogen catalyst effect

Based on the results of the above discussed experiments, the mechanism of catalytic effect 4d-metal alloy (expressed as alloy in reactions (1) and (2)), either extracted (Mo–Ru–Tc–Pd–Rh–Te) or synthetic (Mo–Ru–Pd–Rh), on redox reactions between oxidized radionuclides (expressed as U(VI)O₃(CO₃)₂^{2−} in reactions (1) and (2)) and dissolved hydrogen can be hypothesized by ability of 4d-metals (Ru, Pd and Rh) to catalyze H₂ decomposition to yield chemisorbed H atoms with an intermediate enthalpy of adsorption (reaction (1)) [10]. This then allows the adsorbed H atom to react rapidly as a reductant and desorb thereby maintaining the catalytic reactivity of the surface (reaction (2)):



The stronger catalytic effect of the extracted alloy particles (Exp. 1b) than that synthetic alloy (Exp. 1c) may be explained by the influence of (a) the larger surface area and their nanostructures and/or (b) β-radiation from the fission product alloy particles. In this work it is for the first time demonstrated that β-radiation (electrons e[−]) can enhance the hydrogen catalytic effect of the 4d-metal alloy in the reductive immobilization of radionuclides from the solution saturated with 10% H₂. β-radiation (electrons e[−]) may cause (i) more reducing radicals (such as hydrogen radicals H₂ → H•) than oxidizing radicals, (ii) hydrogen absorbed on 4d-metal alloy surfaces and/or alloy hydride may be activated by radiation. The unique properties of nanostructure materials are attributed not only the surface effects of the nanostructured materials but also to their quantum confinement [24].

4. Summary

From the results of the present and a previous work [6], in which oxidative dissolution of SNF was nearly completely blocked, it can be expected that β-radiation from radioisotopes (⁹⁹Tc, ¹⁰⁷Pd and ¹⁰⁶Ru) contained in the fission product alloy particles, and the overall radiation field from SNF, as well as the atomic level homogeneity and nanostructure of these alloy particles can enhance the catalytic effect of the fission product particles at repository conditions. Considering the much higher partial pressure of H₂ generated at the near field repository conditions, hydrogen induced radionuclide reduction/precipitation under the catalytic effect of fission product alloy particles on the surface of SNF should be one of the most important radionuclide immobilization mechanisms.

Acknowledgments

This work was conducted at Studsvik AB, Sweden and financially supported by Swedish Nuclear Fuel and Waste Management Co. (SKB).

References

- [1] A.P. Novikov, S.N. Kalmykov, S. Utsunomiya, R.C. Ewing, F. Horreard, A. Merkulov, S.B. Clark, B.B. Tkachev, B.F. Myasoedov, *Science* 27314 (2006) 638–641 (no. 5799).
- [2] K. Spahiu, D. Cui, M. Lundström, *Radiochim. Acta* 92 (2004) 626–629.
- [3] H. Kleykamp, *J. Nucl. Mater.* 131 (1985) 463.
- [4] L.E. Thomas, R.E. Einziger, R.E. Woodley, *J. Nucl. Mater.* 166 (1989) 243–251.
- [5] M.E. Broczkowski, J.J. Noel, D.W. Shoesmith, *J. Nucl. Mater.* 346 (2005) 16–23.
- [6] D. Cui, E. Ekeröth, P. Fors, K. Spahiu, *Mater. Res. Soc. Symp. Proc.* 1104 (2008) 87–99.
- [7] D. Cui, J. Low, C.J. Sjöstedt, K. Spahiu, *Radiochim. Acta* 92 (2004) 551–555.
- [8] D. Cui, V.V. Rondinella, K. Spahiu, J.A. Fortner, A.J. Kropf, D.J. Wronkiewicz, Nanostructured hydrogen catalyst extracted from spent nuclear fuel, *Energy Environ. Sci.*, submitted for publication.
- [9] J.M. Schreyer, *J. Am. Chem. Soc.* 77 (2005) 2972–2974.
- [10] H. Li, K. Lee, J. Zhang, in: J. Zhang (Ed.), *PEM Fuel Cell Electrocatalysts and Catalyst Layers*, Springer Verlag London Limited, 2008, p. 149.
- [11] J.A. LaVerne, L. Tandon, *J. Phys. Chem. B* 107 (2003) 13623–13628.
- [12] J.A. LaVerne, *J. Phys. Chem. B* 109 (12) (2005) 5395–5397.
- [13] N.G. Petrik, A.B. Alexandrov, A.I. Vall, *J. Phys. Chem. B* 105 (2001) 5935–5944.
- [14] I. Spitsyn, I.E. Mikhailenko, G.N. Pirogova, Dehydration of Primary Dodecyl Alcohol by Magnesium Sulfate, OSTI Identifier OSTI ID: 4827935, October (11), 1961.
- [15] S. Nobuyuki, W. Yukio, Radioactive catalyst and oxidation–reduction method and apparatus, United States Patent 5,093,302, March 3, 1992.
- [16] R. Guilaumont, T. Fanghanel, T.J. Fuger, Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium, Elsevier, Amsterdam, 2003.
- [17] H. Wanner, *Pure Appl. Chem.* 79 (5) (2007) 875–882.
- [18] D. Cui, K. Spahiu, *Radiochim. Acta* 90 (2002) 623–628.
- [19] T.W. Newton, D.V. Hobart, *J. Nucl. Mater.* 334 (2004) 222–224.
- [20] R.J. Lemire, J. Fuger, H.P. Nistche, J. Potter, J. Rand, K. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, H. Vitorge, H. Wanner, *Chemical Thermodynamics of Neptunium and Plutonium*, Elsevier, Amsterdam, 2001, p. 55.
- [21] J.M. Haschke, V.M. Oversby, *J. Nucl. Mater.* 305 (2002) 187–201.
- [22] J.L. Conca, N. Lu, G. Parker, B. Moore, A. Adams, in: *Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, with an Addendum from ICAM, May, 2000.
- [23] D. Cui, A. Puranen, J. Devoy, J.A. Scheidegger, O. Leupin, P. Wersin, R. Gens, K. Spahiu, *J. Radioanal. Nucl. Chem.* (2009), doi:10.1007/s10967-009-r0328-8.
- [24] A. Henglein, *Chem. Rev.* 89 (1989) 1861.